2011 Sulfur Recovery Symposium
Environmental and Safety Forum

September 14, 2011
2011 Sulfur Recovery Symposium
Sonnenalp Resort, Vail, Colorado
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2011 Sulfur Recovery Symposium Regulatory Update

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Previous Key Regulatory Issues (from 2010)

• NSPS Subpart Ja – No change; administrative stay on flare modifications still in place
• GHG Regulation – Remains in place and effectively unchanged; Current efforts aimed at essentially cutting funding for EPA to implement the programs; the endangerment finding and tailoring rules are continuing to be challenged in court, most notably by Texas
• H₂S TRI Reporting - No change it is still being considered under the same notice
• The New NAAQS (SO₂ and NO₂) – Are in place; states are currently stepping through the modeling process (significant information should be available in 2012)

Refinery Information Collection Request (ICR)

• Massive EPA data collection request under Section 114 of the Clean Air Act
• Huge volume of work compressed into March - August, 2011 schedule
• Requested data for refinery emissions sources includes:
  – Capacity and physical attributes information
  – Emissions information (normal, start-up, shutdown, maintenance and malfunction)
  – Stack parameters
• Requires testing of all crude distillation feed streams to characterize sulfur, chlorides, and metals content
Refinery Information Collection Request (ICR)

- Requires selected facilities to do source (stack tests) for fuel gas systems, **sulfur plants**, coker units, cooling towers, FCCUs, and other refinery processes
- For sulfur plants, sites are to test for sulfur compounds, VOCs, and HAPs
- The testing and survey data will be used to develop new NSPS, MACT, and Residual Risk standards for the refining sector
- May include new GHG limits, HAP limits, and additional limits on sulfur emissions from various locations within a refinery

For more information: [https://refineryicr.rti.org/Home.aspx](https://refineryicr.rti.org/Home.aspx)

TCEQ flare study

- TCEQ (with EPA involvement) has initiated a comprehensive study on flaring
- Findings indicate that some common practices may reduce efficiency below default standards (over steaming, or too much air assist)
- Regulatory changes can be expected – likely impacts:
  - Minimum heating value revised to be based on total integrated heating value (after assist gas is introduced)
  - Revised flare minimization plans
  - Aggregate limits and daily reporting threshold triggers

Cross-State Air Pollution Rule (CSAPR)

- Rule was finalized on July 6, 2011 and published in the Federal Register on August 8, 2011 (76 FR 48208)
- This is a replacement for the Clean Air Interstate Rule which regulates electric utilities
- This rule requires 28 states to significantly improve air quality by reducing power plant emissions that contribute to ozone and/or fine particle pollution in other states

States controlled for both fine particulates (annual SO2 and NOX) and ozone (ozone season NOX) (21 states)
States controlled for fine particulates only (annual SO2 and NOX) (2 states)
States controlled for ozone only (ozone season NOX) (5 states)
States not covered by the Cross-State Air Pollution Rule
Cross-State Air Pollution Rule (CSAPR)

- The rule implements massive reductions in SO₂ emissions in a very short time frame (starting January 1, 2012) – so short that most sites cannot possibly install controls in time to meet limits
- As a result, many utilities will have to look to fuel switching in 2012 and 2013 to try to minimize penalties
- Oil, pet coke-fired and coal utility boilers and power plants will be looking for lower sulfur versions or alternatives to their regular fuel
- Many utilities are looking at switching to NG-fired units

For more information: http://www.epa.gov/airtransport/

H.R. 1204 – The BREATHE Act

BREATHE = Bringing Reductions to Energy’s Airborne Toxic Health Effects

- Introduced to Congress on March 17, 2011
- Amend the Clean AIR Act to:
  - Eliminate the exemption for aggregation of emissions from oil and gas development sources
  - List H₂S as a hazardous air pollutant (HAP) in Section 112
- Forces improved emissions controls on small oil and gas production facilities
- Will force MACT type controls for sources of H₂S emissions
- Supported by: Alaska Wilderness League, Center for Biological Diversity, Earthjustice, Earthworks, Natural Resources Defense Council, Sierra Club, The Wilderness Society

For more information: http://polis.house.gov/Legislation/hr1204.htm
Proposed NSPS Subpart OOOO

- EPA Administrator signed the proposed New Source Performance Standards (NSPS) regulations on July 28, 2011
- Impacts onshore oil and gas processing and transmission and storage facilities
- Natural gas plant regulations NSPS Subparts KKK and LLL are revised and consolidated in the new regulations
- New regulations impacts:
  - Increase the SO₂ emissions control efficiency to 99.9% for NG sulfur recovery units > 5 tpd feed rate with H₂S content ≥ 50%
  - Add leak detection and repair (LDAR) programs for fugitive emissions
  - Storage tanks with ≥ 1 BPD condensate throughput or ≥ 20 BPD crude throughput must have 95% Vapor recovery efficiency or flare controlled
Claus Unit Over-Pressure Potential

- Conditions that disrupt the Process:
  - Process Dead Head Condition:
    • Closed Tail Gas MOV
    • Catalyst/Condenser plugging
    • Condenser filled with sulfur (seal leg or SulTrap plugging)
  - WHB, Condenser or Steam Reheater Tube Leak

- Conditions that result in Loss of Containment:
  - WHB Tube Rupture
  - Thermal Reactor or Fired Reheater Deflagration

WHB Tube Rupture Over Pressure Events

- Over pressure magnitude depends on:
  - WHB operating pressure
  - Size of tubes, size and type of the leak/rupture
  - Downstream equipment causing back pressure

- An industry debate has been on-going for what should represent a “worst-case” failure:
  - History in SRUs has demonstrated that a tube “double-ended” failure is not likely to happen – not per API 521
  - API Taskforce On HRSG Overpressure to provide guidance to API 521 – they have only met 3 times so far

- The incident is not “instant” nor constant:
  - Showing that additional downstream venting can be used as added protection/mitigation
WHB Tube Rupture Over Pressure Events

• The point being: WHB tube failures may or may not be the driver for equipment design criteria
• Therefore: each plant needs to apply the specifics of their process, equipment and acceptable failure conditions to understand this scenario’s impact to the design
• Numerous past paper/presentations available on this subject

Deflagrations

• National Fire Protection Association (NFPA) 68-2007 – Standard on Explosion Protection by Deflagration Venting Annex B addresses the fundamentals of Deflagration
• Deflagration = Propagation of a combustion zone at a velocity less than the speed of sound in the un-reacted medium
  -- Note: Greater than the speed of sound = Detonation
• Deflagration requirements:
  -- A fuel concentration within flammable limits
  -- Oxidant concentration sufficient to support combustion
  -- Presence of an ignition source
Deflagrations – Claus Units

- Ignition source:
  - Spark or flame
  - Conditions facilitating auto-ignition
- Operating thermal reactors are typically in excess of 1800°F:
  - Auto-ignition of Natural gas (in air) = 1076°F
  - Auto-ignition of H₂S (in air) = 500°F
- Claus Units also have iron sulfide present which will auto-ignite when in contact with oxidants:
  - Only one leg of the fire triangle can be eliminated

Deflagrations – Thermal Reactors

- Open path does not really exist:
  - Speed of the deflagration:
    - Burners are designed to deliver the fuel/oxidants in the turbulent flow regime (jet release characteristics)
    - Thermal reactor chamber flows typically remain in the turbulent regime even at un-combusted volumetric flows; Re > 4,000
Deflagrations – Thermal Reactors

- 250 LT/D Unit @ full rate
- 5 ft Zone 1/Zone 2 Choke
- 6 ft Diameter Thermal Reactor
- 355 2½" Diameter Tubes

During severe turndown Re = ~20,000 and Start-up Re = ~6500

Thermal Reactor and WHB are always in the turbulent flow regime*

*Note: Every unit has design specific differences, but flow characteristics are very similar

Deflagrations – Thermal Reactors

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  - Speed of the deflagration:
    - Burners are designed to deliver the fuel/oxidants in the turbulent flow regime (jet release characteristics)
    - Thermal reactor chamber flows typically remain in the turbulent regime even at un-combusted volumetric flows; Re > 4,000
    - Zone 1/Zone 2 restriction (choke or checker wall) significantly aids in accelerating the flame speed
    - This existing turbulence ensures a very fast flame front
  - The high speed of the deflagration causes reflected energy off of the tubesheet back into the thermal reactor
  - Consequence = the WHB tubesheet is a highly restrictive barrier for deflagration de-pressuring
Deflagration – Speeds (Stagnate Conditions)

• Deflagration starts as laminar flame:
  – Laminar flame speed for methane = 0.4 m/sec
  – Laminar flame speed for H₂S = 0.5-1 m/sec*
  – Laminar flame speed for H₂ = 2.65 m/sec
  – Laminar flame speeds increase with increasing gas temperature to 5-10 m/sec

• As flame progresses it folds/wrinkles and is perturbed by obstacles that cause flame to quickly transition to turbulent flame and accelerate. Will happen in just a few inches:
  – Velocities can increase to 500 m/sec

• Based on nominal length of Thermal Reactor, flame progresses full length in less than 0.02 - 0.05 seconds
  * Laminar flame speed estimates courtesy of Nick Roussakis of HEC

Sonic Velocity

• Calculations show that sonic velocity occurs at inlet to WHB tubes after roughly a third of the gas is burnt:
  – Sonic velocity effectively chocks the flow of escaping gases
  – Less than 20% of expanding gas can escape through WHB
  – Accurate calculations intensive and subject to assumptions made

• Testing on vessel (8’ ID x 33’L) with one open end yielded deflagration pressures of >100 psig due to mixing through choke ring*

* Gas Explosion Handbook; Bjerketvedt, Bakke, & van Wingerden
Deflagration Potential

- During Start-up:
  - Unlit burners can place sufficient amounts of fuel and air into the thermal reactor to reach LFL conditions
  - Conditions facilitating auto-ignition will be present during hot restarts
  - Many ignition system components can malfunction

- Undetected flame-outs:
  - \( \text{H}_2\text{S} \) and Oxidant levels already at LFL conditions
  - Unlit burner entry temperature is 300\(^\circ\)F below auto-ignition temperature – Zone 1 accumulation can occur
  - Flame Scanner imperfections can lead to this condition
Deflagration Potential

- Large diameter thermal reactors can have a large gas volume accumulate before making wall contact/reaching auto-ignition conditions
- A cold chamber can essentially reach gas full conditions before auto-ignition temperature is achieved:
  - Radiant heat is proportion to temperature to the 4th power
  - At 1000°F the radiant heat is only 12% of the value at 2000°F and at 750°F the radiant heat is at 6%
  - At these lower temperatures, it takes 2-4 seconds to heat up the gas in Zone 1 and it only takes 0.1-0.3 seconds to fill Zone 1
- A purge malfunction can cause air/O₂ to come in contact with a significant H₂S/sulfur vapor cloud where the UFL can be reached at auto-ignition conditions

Deflagration Potential – Flame Scanner Imperfections

- Refractory back glow provides sufficient IR and any gas movement can simulate the “flame flicker”
- H₂S readily absorbs UV
- False trip over-correction in gain settings can lead to insufficient sensitivity to flame loss
- Changing compositions of the acid gas can fluctuate the IR and UV emitted by the burner
- Cold startup vs. hot startup present very different radiant light profiles that challenge the scanners:
- Although there have been significant improvements in the technology and reliability – they are not infallible!
Deflagration Pressure

- Deflagration pressure has the same relation as the ideal gas law:

\[ P = \frac{nRT}{V} \]

- Maximum deflagration pressure test data (in air):

<table>
<thead>
<tr>
<th>Fuel Component</th>
<th>( P_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From NFPA 68 Table E.1</td>
</tr>
<tr>
<td>Methane</td>
<td>7.1 barg (103.0 psig)</td>
</tr>
<tr>
<td>Ethane</td>
<td>7.8 barg (113.1 psig)</td>
</tr>
<tr>
<td>Propane</td>
<td>7.9 barg (114.6 psig)</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>7.4 barg (107.3 psig)</td>
</tr>
</tbody>
</table>

Deflagration Pressure

- Deflagration test pressures can be converted to pressure rise ratios as follows:

\[ R_{PR} = \frac{(P_{\text{max}} + P_{\text{atm}})}{(P_{\text{initial}})} \]

- Completing the calculations:

<table>
<thead>
<tr>
<th>Fuel Component</th>
<th>( R_{PR} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>8.0</td>
</tr>
<tr>
<td>Ethane</td>
<td>8.7</td>
</tr>
<tr>
<td>Propane</td>
<td>8.8</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>8.3</td>
</tr>
</tbody>
</table>
**Deflagration Pressure**

- Typical final deflagration pressures (air only):
  - Methane $P_{\text{initial}} = 1.1$ psig (start-up)
  - $H_2S$ $P_{\text{initial}} = 9.3$ psig (full rate)

  \[ P_{\text{def}} = R_{PR}(P_{\text{initial}} + P_{\text{atm}}) - P_{\text{atm}} \]

<table>
<thead>
<tr>
<th>Fuel Component</th>
<th>Claus Unit Deflagration Pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane*</td>
<td>111.7</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>186.2</td>
</tr>
</tbody>
</table>

*Natural gas may yield slightly lower deflagration pressures due to possible inert components

- However, we know that acid gas is not pure $H_2S$
- And many of today’s operations are $O_2$ enriched

**Deflagration Pressure**

- An example amine acid gas composition
- BR&E’s Promax® software was used to create process simulations of the combustion of this amine acid gas with air and $O_2$ enriched air environments
- The simulated combustion temperature and moles of combustion product were then used to calculate the deflagration pressure using the ideal gas law

<table>
<thead>
<tr>
<th>Species</th>
<th>Mol%</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>0.43</td>
<td>0.38</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>10.50</td>
<td>9.27</td>
</tr>
<tr>
<td>$C_2H_6$</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>$C_3H_8$</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>$H_2S$</td>
<td>78.29</td>
<td>84.14</td>
</tr>
<tr>
<td>COS</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$C_2H_4$</td>
<td>0.09</td>
<td>0.13</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>10.65</td>
<td>6.05</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>Mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°F)</td>
<td>139</td>
</tr>
<tr>
<td>$P$ (psig)</td>
<td>11.5</td>
</tr>
<tr>
<td>Mol Weight</td>
<td>33.39</td>
</tr>
<tr>
<td>Density (lb/ft³)</td>
<td>0.1366</td>
</tr>
</tbody>
</table>
Deflagration Pressure

\[ \frac{P_1 V_1}{z_1 n_1 R T_1} = \frac{P_2 V_2}{z_2 n_2 R T_2} \]

- \( P_1 \) = Initial operating pressure of Thermal Reactor, psia
- \( P_2 \) = Deflagration pressure, psia
- \( V_1 = V_2 \) = Fixed volume
- \( z_1 \) = Correction factor for the initial conditions
- \( z_2 \) = Correction factor for the deflagration conditions
- \( T_1 \) = Initial temperature of non-combusted acid gas and air (or \( O_2 \) enriched air), \(^\circ\)R
- \( T_2 \) = Deflagration temperature from simulation (maximum possible), \(^\circ\)R
- \( n_1 \) = Initial moles of amine gas and air (or \( O_2 \) enriched air) from simulation
- \( n_2 \) = Moles of combustion products from simulation

Rearranged and simplified:

\[ P_2 = \frac{P_1 z_2 n_2 T_2}{z_1 n_1 T_1} \]

### Deflagration Pressure

<table>
<thead>
<tr>
<th>Fuel/Oxidant</th>
<th>Deflagration Pressure (psig)</th>
<th>Pressure Rise Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid gas in air</td>
<td>114.7</td>
<td>5.4</td>
</tr>
<tr>
<td>Acid gas in enriched air (30% ( O_2 ))</td>
<td>136.4</td>
<td>6.3</td>
</tr>
<tr>
<td>Acid gas in enriched air (40% ( O_2 ))</td>
<td>158.4</td>
<td>7.2</td>
</tr>
<tr>
<td>Acid gas in enriched air (50% ( O_2 ))</td>
<td>175.6</td>
<td>7.9</td>
</tr>
<tr>
<td>Acid gas in enriched air (60% ( O_2 ))</td>
<td>189.6</td>
<td>8.5</td>
</tr>
<tr>
<td>Acid gas in enriched air (80% ( O_2 ))</td>
<td>211.4</td>
<td>9.4</td>
</tr>
<tr>
<td>Acid gas in 100% ( O_2 )</td>
<td>228.8</td>
<td>10.1</td>
</tr>
</tbody>
</table>
Deflagration Protection Methods

• Deflagration Venting:
  – Devise to relieve the pressure by venting the vessel contents directly to the atmosphere
  – Addressed in NFPA 68

• NFPA 68 requires it to be done in a safe manner:
  – Thermal Reactor release temperature would exceed 2000°F
  – This would result in a significant toxic gas release
  – Obviously not recommended nor NFPA complaint for this service

Deflagration Protection Methods

• NFPA 69 – Explosion Prevention Systems:

<table>
<thead>
<tr>
<th>Method</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deflagration Prevention by Oxidant Concentration Reduction</td>
<td>7</td>
</tr>
<tr>
<td>Deflagration Prevention by Combustible Concentration Reduction</td>
<td>8</td>
</tr>
<tr>
<td>Pre-deflagration Detection and Control of Ignition Sources</td>
<td>9</td>
</tr>
<tr>
<td>Deflagration Control by Suppression</td>
<td>10</td>
</tr>
<tr>
<td>Deflagration Control by Active Isolation</td>
<td>11</td>
</tr>
<tr>
<td>Deflagration Control by Passive Isolation</td>
<td>12</td>
</tr>
<tr>
<td>Deflagration Control by Pressure Containment</td>
<td>13</td>
</tr>
<tr>
<td>Passive Explosion Suppression Using Expanded Metal Mesh or Polymer Foams</td>
<td>14</td>
</tr>
</tbody>
</table>
Explosion Prevention (NFPA 69)

- Chapters 9, 10, 11, 12 and 14 don’t apply to Sulfur Recovery.

<table>
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<td>Passive Explosion Suppression Using Expanded Metal Mesh or Polymer Foams</td>
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</tr>
</tbody>
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Explosion Prevention (NFPA 69)

- Chapters 7 and 8 discuss Safety Instrumented Systems
- The following are the Design Considerations for a system intended to reduce the oxidant concentration (Chapter 7) and fuel (Chapter 8):
  1. Required reduction in oxidant (or fuel) concentration
  2. Variations in the process, process temperature and pressure, and materials being processed
  3. Source purge gas supply and equipment installation
  4. Compatibility of the purge gas with the process
  5. Operating controls
  6. Maintenance, inspection, and testing
  7. Personnel exposure due to leakage of purge gas to surrounding areas
  8. Need for breathing apparatus by personnel
  9. Reduced effectiveness of purge gas due to equipment leakage and loss through vents
Explosion Prevention (NFPA 69)
Chapters 7 and 8 - Other Requirements

• The following Information is required for monitoring and control shall be compiled and documented. This shall include, but not be limited to, the following information:
  1. Monitoring and control objectives
  2. Monitored and controlled areas of the process
  3. Dimensioned drawings of the process with the following information:
     a. Equipment make and model if available, including volumes and diameters and design strength
     b. Plan and elevation views with flows indicated
  4. Startup, normal, shutdown, temporary operations, and emergency shutdown process conditions and ranges for the following factors:
     a. Flow
     b. Temperature
     c. Pressure
     d. Oxidant concentration
  5. Process flow diagram and description
  6. Ambient temperature in process area
  7. Process interlocks
• The owner or operator shall be responsible for the maintenance of the system after installation and acceptance based on procedures provided by the vendor.
• Maintenance records shall be retained for inspection by the authority having jurisdiction
• The owner or operator shall be responsible for periodic inspection of the system by personnel trained by the system manufacturer.
• Required levels of oxidant or fuel concentration - owner or operator documents that their system achieves the levels and that maintenance and inspection are completed on a regular basis to confirm the system is operating correctly.

Explosion Prevention (NFPA 69)
Chapters 7 and 8

• Requires a sophisticated SIS addressing start-up, normal, shutdown, temporary operations, and emergency shutdown process conditions/ranges for the these factors:
  a. Flow    d. Oxidant concentration
  b. Temperature  e. Fuel Concentration
  c. Pressure    f. Inert Purging

• Oxidants act as a fuel in the Claus Unit equipment due to impregnated sulfur and iron sulfide build-up
• Continuous flame stability is essential which is ensured only through flame scan which is not full-proof
Explosion Prevention (NFPA 69)

- Chapter 13 addresses **Deflagration Control by Pressure Containment** *(added in 1986)*
- If the equipment is designed to withstand a deflagration then the intent has been met
- The user shall determine whether permanent deformation of the protected enclosure, as a result of a potential deflagration, can be accepted
- Best acceptable practice for assuring safe over pressure protection
- Note – “true” NFPA 69 Chapter 13 addresses systems in which the oxidant is air

Equipment Design Requirements

\[ P_{mawp} \geq \frac{[R_{PR}(P_i + 14.7) - 14.7]}{\left(\frac{3}{2}\right)F_u} \]

- **\( P_{mawp} \)** = enclosure design pressure (psig) according to ASME Boiler and Pressure Vessel Code *(maximum available working pressure)*
- **\( R_{PR} \)** = dimensionless pressure rise ratio
- **\( P_i \)** = maximum initial pressure at which combustible atmosphere exists (psig)
- **\( F_u \)** = ratio of ultimate stress of the enclosure to the allowable stress of the enclosure according to ASME Boiler and Pressure Vessel Code – *used if permanent deformation but not rupture is acceptable. Yield stress is used in place of ultimate stress if deformation is not acceptable.*

- For SA-516-70 plate steel:
  - Minimum tensile strength is 70,000 psi
  - Allowable stress at 650°F is 18,800 psi
  - **\( F_u = 70,000 \text{ psi}/18,800 \text{ psi} \)**
**Equipment Design Requirements**

**(SA -516-70 Plate Steel Vessels)**

\[ P_i = 9.3 \text{ psig (full rate)} \]

<table>
<thead>
<tr>
<th>Fuel/Oxidant</th>
<th>( R_{RP} )</th>
<th>( P_{mawp} ) (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid gas in air</td>
<td>5.4</td>
<td>46.2</td>
</tr>
<tr>
<td>Acid gas in enriched air (30% ( O_2 ))</td>
<td>6.3</td>
<td>54.9</td>
</tr>
<tr>
<td>Acid gas in enriched air (40% ( O_2 ))</td>
<td>7.2</td>
<td>63.8</td>
</tr>
<tr>
<td>Acid gas in enriched air (50% ( O_2 ))</td>
<td>7.9</td>
<td>70.8</td>
</tr>
<tr>
<td>Acid gas in enriched air (60% ( O_2 ))</td>
<td>8.5</td>
<td>76.4</td>
</tr>
<tr>
<td>Acid gas in enriched air (80% ( O_2 ))</td>
<td>9.4</td>
<td>85.2</td>
</tr>
<tr>
<td>Acid gas in 100% ( O_2 )</td>
<td>10.1</td>
<td>92.2</td>
</tr>
<tr>
<td>Natural gas in air (( P_i = 1.0 ) psig)</td>
<td>7.2</td>
<td>39.6</td>
</tr>
</tbody>
</table>

*Source = “Expllosion Limits of \( H_2S/CO_2/\text{Air} \) and \( H_2S/N_2/\text{Air} \)” by Robert Pahl and Kai Holtappels, 2005, WILEY-VCH, Verlag GmbH & Co. KGaA, Weinheim*

**Equipment Design Requirements**

**(SA -516-70 Plate Steel Vessels)**

- One last plausible case to consider:
  - Amine acid gas at the upper flammability limit in oxygen
  - The upper flammability limit of \( H_2S \), at ambient conditions, is 49.8 mole%*
  - \( P_i = 9.3 \) psig
  - SA-516-70 Plate Steel Vessel

<table>
<thead>
<tr>
<th>( P_{def} ) (psig)</th>
<th>( R_{RP} )</th>
<th>( P_{mawp} ) (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>198.5</td>
<td>8.3</td>
<td>74.0</td>
</tr>
</tbody>
</table>

*Source = “Expllosion Limits of \( H_2S/CO_2/\text{Air} \) and \( H_2S/N_2/\text{Air} \)” by Robert Pahl and Kai Holtappels, 2005, WILEY-VCH, Verlag GmbH & Co. KGaA, Weinheim*
Conclusions and Summary

- Required SRU/TGTU MAWP can be set based on either WHB tube rupture or deflagration
- Engineering analysis required to determine what is the controlling case – don’t assume which is controlling based on other designs!
- NFPA 69 Chapter 13 was added in 1986:
  - Units built before 1986 may not be designed for deflagration pressure. NFPA 69 is not retroactive to old units, but how much revamp work is allowed before it needs to be considered?
  - Even newer already pressure rated thermal reactors should be re-evaluated when upgrading to higher levels of O₂ enrichment

Other Key Considerations

- NFPA 85 Boiler and Combustion Systems Hazardous Code and NFPA 86 Standard for Ovens and Furnaces do not really address the unique nature of an SRU burner:
  - NFPA 85 is the best that is available but needs to be applied with common sense and understanding of the operation of an SRU
- API Recommended Practice (RP) 520:
  - Get involved in API Taskforce On HRSG Overpressure
  - They need data and input!
Thank you for your attention

Appendix A: Simulation Results

<table>
<thead>
<tr>
<th>Fuel/Oxidant Case</th>
<th>$P_1$ (psia)</th>
<th>$z_1$</th>
<th>$T_1$ (°R)</th>
<th>$T_2$ (°R)</th>
<th>$n_1$ (moles)</th>
<th>$n_2$ (moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid gas in air</td>
<td>24.007</td>
<td>0.9995</td>
<td>648.74</td>
<td>3706.6</td>
<td>669.00</td>
<td>630.84</td>
</tr>
<tr>
<td>Acid gas in enriched air (30% O$_2$)</td>
<td>24.007</td>
<td>0.9994</td>
<td>663.29</td>
<td>4491.1</td>
<td>485.29</td>
<td>450.81</td>
</tr>
<tr>
<td>Acid gas in enriched air (40% O$_2$)</td>
<td>24.007</td>
<td>0.9989</td>
<td>644.2</td>
<td>5034.6</td>
<td>384.25</td>
<td>354.07</td>
</tr>
<tr>
<td>Acid gas in enriched air (50% O$_2$)</td>
<td>24.007</td>
<td>0.9984</td>
<td>627.9</td>
<td>5412.8</td>
<td>325.28</td>
<td>298.61</td>
</tr>
<tr>
<td>Acid gas in enriched air (60% O$_2$)</td>
<td>24.007</td>
<td>0.9980</td>
<td>613.9</td>
<td>5661.3</td>
<td>288.39</td>
<td>264.15</td>
</tr>
<tr>
<td>Acid gas in enriched air (80% O$_2$)</td>
<td>24.007</td>
<td>0.9971</td>
<td>590.7</td>
<td>6076.7</td>
<td>246.74</td>
<td>225.24</td>
</tr>
<tr>
<td>Acid gas in 100% O$_2$</td>
<td>24.007</td>
<td>0.9962</td>
<td>571.4</td>
<td>6335.8</td>
<td>222.60</td>
<td>202.29</td>
</tr>
<tr>
<td>Acid gas at UFL in O$_2$</td>
<td>24.007</td>
<td>0.9998</td>
<td>578.5</td>
<td>6336.9</td>
<td>157.22</td>
<td>157.94</td>
</tr>
</tbody>
</table>
About the Authors:

Everyday | Excellence

**Philip Oberbroeckling, P.E.** is a Consulting Engineer in LyondellBasell’s Refining Process Engineering Group providing Sulfur Recovery technical support to the Houston and Berre, France Refineries. Philip is the Lead Process Engineer for all sulfur recovery capital projects at Houston including the currently ongoing Oxygen Enrichment Expansion. Over Philip’s 21 years of service in the Refining Industry, he has had numerous engineering and management positions in Process, HSSE and Operations including a 5-year tenure as the Operations Superintendent of the Houston Refinery’s 1000 LT/D Sulfur Recovery Facility. Philip holds a Bachelor of Science degree in Chemical Engineering from Iowa State University and is a registered Professional Engineer in the states of Montana and Texas. Philip has authored over 30 technical papers and presentations on topics related to the Sulfur Recovery and the Refining Industries. Philip is a member of the Sulfur Recovery Symposium Technical Advisory Committee and the Founder and Chairman of the Environmental and Safety Committee.

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